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(54) CATALYST FOR PURIFYING EXHAUST GAS

(57)Abstract:

PURPOSE: To obtain a ternary catalyst for an internal combustion engine high in durability.

CONSTITUTION: A catalyst carrier is coated with a mixture consisting of catalytically active components prepared by supporting platinum and/or palladium on cerium oxide stabilized by rare earth metal (excepting zirconium and cerium) and zirconium and refractory inorg. oxide based on activated alumina and, thereafter, rhodium and/or rhodium and a platinum group metal are further supported on the carrier to obtain the objective catalyst for purifying exhaust gas. Since platinum and/or palladium are preliminarily supported on stabilized cerium oxide, the sintering of platinum and palladium is suppressed and catalytic activity can be kept long.

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The catalyst for exhaust gas clarification characterized by coming to support a rhodium and/or a rhodium, and a platinum metal further after making catalyst support cover with a zirconium, or the rare earth metal and zirconium except a cerium the mixture which turns into cerium oxide by which heat stabilization was carried out from the catalytic activity component which supported platinum and/or palladium, and the fireproof inorganic oxide which made the activated alumina the subject.

[Claim 2] The catalyst for exhaust gas clarification according to claim 1 currently supported by the cerium oxide with which heat stabilization of at least 30% of the weight or more of the total amount of the platinum currently supported and/or palladium was carried out.

[Claim 3] The catalyst for exhaust gas clarification according to claim 1 whose amount of support of a rhodium the amount of support of platinum and/or palladium is 0.1–5.0g/l. per unit capacity of a catalyst, and is 0.01–1.0g/l.

[Claim 4] The catalyst for exhaust gas clarification according to claim 1 whose amount of support of a rhodium the amount of support of platinum and/or palladium is 0.3–3.0g/l. per unit capacity of a catalyst, and is 0.05–0.5g/l.

[Claim 5] 50% of the weight or more of a rhodium is the catalyst for exhaust gas clarification according to claim 1 currently supported within 40 micrometers from the front face of the layer which consists of a fireproof inorganic oxide covered by catalyst support.

[Claim 6] The catalyst for exhaust gas clarification according to claim 1 10–200g, and whose fireproof inorganic oxide the cerium oxide by which heat stabilization was carried out is 80–300g per 1l. of catalyst support.

[Claim 7] It is the catalyst for exhaust gas clarification according to claim 1 whose specific surface area the mean particle diameter of the cerium oxide by which heat stabilization was carried out is 10 micrometers or less, and is more than 20m² / g.

[Claim 8] The cerium oxide by which heat stabilization was carried out is a catalyst for exhaust gas clarification according to claim 1 in which it is the mixture of cerium oxide, a zirconic acid ghost, and the rare earth oxide except cerium oxide, and at least the part exists as a multiple oxide or the solid solution.

[Claim 9] The multiple oxide or the solid solution of cerium oxide, a zirconic acid ghost, and rare earth oxide is a catalyst for exhaust gas clarification according to claim 5 constituted so that a zirconium may be served as to 0.05 to 0.35 by the remainder and the sum total of zero to 0.30, a zirconium, and a rare earth metal may serve as [a rare earth metal] a cerium respectively at an atomic rate 0.05–0.55.

[Claim 10] A fireproof inorganic oxide is a catalyst for exhaust gas clarification according to claim 1 which are an activated alumina, the activated alumina by which heat stabilization was carried out, the oxide of a rare earth metal, and the oxide of alkaline earth metal.

[Claim 11] An activated alumina is a catalyst for exhaust gas clarification according to claim 1 whose mean particle diameter is 10 micrometers or less and whose specific surface area it is kinds of gamma-alumina, delta-alumina, and theta alumina, or such mixture, and is more than 50m² / g.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the catalyst for exhaust gas clarification which removes simultaneously the carbon monoxide (CO), the hydrocarbon (HC), and nitrogen oxides (NOx) which are the injurious ingredients contained in the exhaust gas from internal combustion engines, such as an automobile, about the catalyst for exhaust gas clarification.

[0002]

[Description of the Prior Art] Conventionally, in the three way component catalyst which removes simultaneously the carbon monoxide, the hydrocarbon, and nitrogen oxides which are the injurious ingredients in the exhaust gas discharged by the internal combustion engine, the cerium oxide which has oxygen storage effect mainly for platinum group metals, such as platinum and a rhodium, and the improvement in low-temperature activity is used.

[0003] Such a conventional catalyst for exhaust gas clarification performs coating by the slurry of an activated alumina, sinks into a cerium solution after that, and is performing impregnation support to integral-construction mold monolith support using platinum-group-metals content solutions, such as platinum and a rhodium, after that further, there is an inclination for the installation of these catalysts to be carried out directly under [more near an engine] a manifold recently — moreover, the elevated-temperature thermal resistance of a catalyst has been more greatly required by lifting of the exhaust gas temperature at the time of high-speed operation etc.

[0004] However, the catalyst containing conventional platinum group metals and cerium oxide tends to deteriorate in an elevated temperature. In order to raise the elevated-temperature thermal resistance of a catalyst for this reason, the oxide of a rare earth metal or alkaline earth metal is added. Moreover, if a long duration activity is carried out at an elevated temperature, the so-called sintering which a platinum particle condenses and causes grain growth will occur, and the clarification engine performance will deteriorate remarkably. The catalyst which supported platinum on cerium oxide for the sintering control of platinum to JP,5-20435,Y is indicated.

[0005]

[Problem(s) to be Solved by the Invention] However, although the above-mentioned conventional three way component catalyst showed the good 3 yuan activity for purifying three components of CO, HC, and NOx in the first stage, it was not necessarily able to say that it was enough in endurance or thermal resistance in the large part of fluctuation of an elevated temperature [like / directly under a manifold], and a gas ambient atmosphere component.

[0006] Therefore, in the catalyst which uses platinum and/or palladium, and a rhodium as a catalyst component, simultaneously, this invention is stabilized, purifies three components of CO, HC, and NOx over a long period of time, from the first stage, and is to offer the catalyst which can maintain the endurance in an elevated temperature.

[0007]

[Means for Solving the Problem] The catalytic activity component which supported platinum and/or palladium with the zirconium, or the rare earth metal and zirconium except a cerium to the cerium oxide by which heat stabilization was carried out as a result of inquiring wholeheartedly, in order that this invention person may solve this technical problem, After making catalyst support cover the mixture which consists of a fireproof inorganic oxide which made the activated alumina the subject, Furthermore, it comes to complete a header and this invention for the catalyst engine performance improving compared with the catalyst in which the catalyst for exhaust gas clarification which comes to support a rhodium and/or a rhodium, and a platinum metal contains platinum and/or conventional palladium, and a conventional rhodium.

[0008] As for the amount of support of the platinum and/or palladium which are supported by a catalytic activity component and the fireproof inorganic oxide, it is desirable that it is 0.1-5.0g/l. per unit capacity of a catalyst. When the amount of support of platinum and/or palladium is less than 0.1g/l. per unit capacity, there is a possibility that sufficient clarification engine performance may not be obtained. Moreover, even if the amount of support of platinum and/or palladium exceeds l. in 5.0g /per unit capacity conversely, only the effectiveness of balancing the amount of support is not acquired. Especially, the case where the amount of support of platinum and/or palladium is 0.3-3.0g/l. per unit capacity is more more desirable than the field of catalytic activity and cost.

[0009] Moreover, it is desirable that 30% of the weight or more of the total amount of support of the platinum supported by catalyst support and/or palladium is supported by the heat stabilization cerium oxide. When the amount of support of platinum and/or palladium is less than 30%, since the sintering control at the time of an elevated temperature is not enough, it is not desirable. As for the amount of support of the rhodium supported by catalyst ****, it is desirable that it is 0.01-1.0g/l. per unit volume of a catalyst. It has a possibility that sufficient catalytic activity may not be acquired, when the amount of support of a rhodium is less than 0.01g/l. per unit volume. Moreover, even if the amount of support of a rhodium exceeds l. in 1.0g /per unit volume conversely, only the effectiveness of balancing the amount of support is not acquired. Especially when the amount of support of a rhodium is 0.05-0.5g/l. per unit volume, it is more desirable in respect of catalytic activity and cost.

[0010] As a fireproof inorganic oxide, the oxide of alkaline earth metal, such as an oxide of rare earth metals, such as an activated

alumina by which heat stabilization was carried out with an activated alumina, silicon, and/or those oxides, and a lanthanum, magnesium, and barium, is desirable. These fireproof inorganic oxides have a desirable thing with a large specific surface area with a small particle size. In the case of an activated alumina, more than 50m² / g of mean particle diameter are [10 micrometers or less and specific surface area] good.

[0011] As for a fireproof inorganic oxide, specifically, what makes an activated alumina a subject is good. As for a fireproof inorganic oxide, what contains more than a kind of the oxide of a rare earth metal or a compound, the oxide of alkaline earth metal, or a compound in an activated alumina is good more preferably. Moreover, as for an activated alumina, what consists of kinds of gamma-alumina, delta-alumina, and theta alumina or such mixture, and contains a kind of silicon, a rare earth metal, and alkaline earth metal or its compound still more preferably for heat stabilization is good. [0012] Heat stabilization of the cerium oxide by which heat stabilization was carried out is carried out by the zirconium, or the rare earth metal and zirconium except a cerium. This cerium oxide (henceforth a heat stabilization cerium oxide) by which heat stabilization was carried out can be adjusted by the following approaches. However, a heat stabilization cerium oxide is not limited to especially the adjustment approach shown here. The approach of supporting a water-soluble zirconium salt and/or the rare earth metal salt except a cerium to commercial cerium oxide as the adjustment approach of this heat stabilization cerium oxide, the cerium salt melted in water, a zirconium salt, and/or the rare earth metal salt except a cerium can be mixed, and the approach of supporting to a fireproof inorganic oxide etc. can be raised after desiccation after mixing the rare earth metal except the approach of calcinating, a water-soluble cerium salt, a zirconium salt, and/or a cerium. In addition, 500 degrees C of baking are made by heating for about 5 hours for example, in air. By any approach, especially each salt of the rare earth metal except the cerium, zirconium, and cerium to be used is not limited, but can use a commercial nitrate, acetate, a sulfate, a chloride, etc.

[0013] The heat stabilization cerium oxide adjusted by said adjustment approach is the mixture of cerium oxide, a zirconic acid ghost, and the rare earth oxide except cerium oxide, and at least the part exists as a multiple oxide or the solid solution. When the whole is made into 100 atoms %, as for the rate of the atom of rare earth elements other than the cerium atom which constitutes heat stabilization cerium oxide, a zirconium atom, and a cerium atom, it is desirable that the atom of rare earth elements other than five to 35 atom % and a cerium atom serves as zero to 30 atom %, and the remainder serves as [a zirconium atom] a cerium atom.

[0014] Even if it calcinates in air the heat stabilization cerium oxide adjusted by the above-mentioned approach at 900 degrees C for 5 hours, specific surface area is more than 20m² / g. In addition, if commercial cerium oxide is calcinated on these conditions, specific surface area will deteriorate in below 10m² / g. As for each component mixed, it is desirable like the above that 10-200g, and a fireproof inorganic oxide are blended per 1L of catalysts and for a heat stabilization cerium oxide at a rate (80-300g).

[0015] Although catalyst **** which had the mixture of a catalytic activity component and a fireproof inorganic oxide covered makes a catalyst metal support further, they are platinum metals, such as the platinum and/or palladium which were already supported by heat stabilization cerium oxide as the catalyst metal, and a rhodium, and other noble metals, and it is desirable one sort or to use two or more sorts and to support.

[0016]

[Function and Effect of the Invention] Since platinum and/or palladium were supported on the heat stabilization cerium oxide, this invention was able to control sintering which was not able to be solved conventionally. Therefore, it is an elevated temperature [like / directly under a manifold], and endurance and thermal resistance have been greatly improved also in the large location of fluctuation of a gas ambient atmosphere.

[0017] Moreover, compared with the platinum and/or palladium on the activated alumina in the conventional approach, the rate of clarification of palladium [the platinum on heat stabilization cerium oxide and/or] of CO and a NOx component improved. Moreover, as compared with the platinum and palladium on the cerium oxide by which heat stabilization is not carried out, endurance of palladium [the platinum and palladium] on the cerium oxide in which this invention carried out heat stabilization is improving remarkably. Moreover, clarification of CO and NOx which excelled [oxidization / in which this invention of this invention carried out heat stabilization / cerium] in a small amount of platinum and palladium more compared with what was mixed in the cerium salt and oxidized platinum and palladium was completed.

[0018]

[Example] Hereafter, an example explains concretely.

(Example 1) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0019] Next, the dinitrodiammone platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 2 % of the weight. Next, the coat of the slurry which becomes the monolith support with 400 cels / in², a diameter [of 80mm], and a die length of 95mm made from cordierite from the multiple oxide powder of a platinum content zirconium cerium, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and platinum, the cerium, the zirconium, and the activated-alumina content layer were formed in the monolith support made from cordierite.

[0020] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 1 was acquired. A catalyst presentation is shown in a table 1. Moreover, the blending ratio of coal of platinum, a cerium, and a rhodium was investigated for the enveloping layer cross section of this catalyst 1 by EPMA (electron probe microanalysis).

Consequently, the rhodium existed in the range of 40 micrometers from the front face of an enveloping layer. Moreover, it became clear that platinum and a cerium have the presentation to which the peak etc. was similar. It turns out that platinum and a cerium approach mutually and exist from this.

[0021] (Example 2) The catalyst 1 was acquired like the example 1 except having changed the mole ratio of a cerium/zirconium into

19/1, and having changed gamma-alumina powder into the gamma-alumina powder containing La of 3 atom %. A catalyst presentation is shown in a table 1.

(Example 3) The catalyst 1 was acquired like the example 1 except having changed the mole ratio of a cerium/zirconium into 2/1, and having changed gamma-alumina powder into the gamma-alumina powder containing Ba of 3 atom %. A catalyst presentation is shown in a table 1.

[0022] (Example 4) 2.0% of the weight of the platinum content in the platinum content zirconium cerium multiple oxide of an example 1 was carried out to 1.0% of the weight, and the enveloping layer which becomes monolith support from a platinum content zirconium cerium multiple oxide and an activated alumina like an example 1 was formed.

[0023] Furthermore, monolith support with this enveloping layer was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 4 was acquired. A catalyst presentation is shown in a table 1.

(Example 5) 2.0% of the weight of the platinum content in the platinum content zirconium cerium multiple oxide of an example 1 was carried out to 0.6% of the weight, and the enveloping layer which becomes monolith support from a platinum content zirconium cerium multiple oxide and an activated alumina like an example 1 was formed.

[0024] Furthermore, monolith support with this enveloping layer was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution after that, the rhodium was supported, and the catalyst 5 was acquired. A catalyst presentation is shown in a table 1.

(Example 6) By 5 micrometers of mean diameters, the cerium oxide, oxy-zirconium-nitrate solution, and nitric-acid yttrium solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out with the zirconium and the yttrium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out with this zirconium and yttrium was 5/1/0.2 in the mole ratio of a cerium / zirconium / yttrium.

[0025] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out with the above-mentioned zirconium and the yttrium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium yttrium cerium oxide was obtained. The platinum content in this platinum content zirconium yttrium cerium multiple oxide was 2 % of the weight.

[0026] Next, the coat of the slurry which becomes the monolith support with 400 cels / in², a diameter [of 80mm], and a die length of 95mm made from cordierite from the multiple oxide powder of a platinum content zirconium yttrium cerium, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, an yttrium, and an activated alumina in monolith support was formed.

[0027] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 6 was acquired. A catalyst presentation is shown in a table 1.

(Example 7) By 5 micrometers of mean diameters, the cerium oxide, oxy-zirconium-nitrate solution, and nitric-acid ytterbium solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium and the ytterbium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium and ytterbium was 5/1/0.2 in the mole ratio of a cerium / zirconium / ytterbium.

[0028] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the zirconium and the ytterbium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium ytterbium cerium oxide was obtained. The platinum content in this platinum content zirconium ytterbium cerium multiple oxide was 2 % of the weight.

[0029] Next, the coat of the slurry which becomes the monolith support with 400 cels / in², a diameter [of 80mm], and a die length of 95mm made from cordierite from the multiple oxide powder of a platinum content zirconium ytterbium cerium, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, an ytterbium, and an activated alumina in monolith support was formed.

[0030] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 7 was acquired. A catalyst presentation is shown in a table 1.

(Example 1 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from the multiple oxide powder, the gamma-alumina powder, hydrated alumina, and pure water of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium-zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst A was acquired. A catalyst presentation is shown in a table 1. The blending ratio of coal of platinum and a rhodium was investigated for the enveloping layer cross section of this catalyst A by EPMA. Consequently, it was distributed over the range of 100 micrometers from the front face of an enveloping layer, and the rhodium was distributed over the range of 40 micrometers by platinum from the front face of an enveloping layer.

[0031] (Example 2 of a comparison) 2.0% of the weight of the platinum content in the platinum content zirconium cerium multiple oxide of an example 1 was carried out to 0.4% of the weight, and the layer which becomes the monolith support made from cordierite from platinum, a cerium, a zirconium, and an activated alumina like an example 1 was formed.

[0032] Furthermore, this monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst B was acquired. A catalyst presentation is shown in a table 1.

(Example 3 of a comparison) The dinitrodiammine platinum solution was added and calcinated [dried and] to activated-alumina powder, and the platinum content activated alumina was obtained. The platinum content in this platinum content activated alumina was 2.0 % of the weight.

[0033] Next, the coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from a platinum content activated alumina, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, and an activated alumina in the monolith support made from cordierite was formed.

[0034] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst C was acquired. A catalyst presentation is shown in a table 1.

(Example 4 of a comparison) The dinitrodiammine platinum solution was added and calcinated [dried and] to cerium oxide powder, and platinum content cerium oxide was obtained. The platinum content in this platinum content cerium oxide was 2.0 % of the weight.

[0035] Next, the coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from platinum content cerium oxide, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, and an activated alumina in the monolith support made from cordierite was formed.

[0036] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst D was acquired. It is shown in the catalyst presentation table 1.

[0037]

[A table 1]

触媒	アルミナのコート量(g/リットル)	Pt/Pd担持量(g/リットル)〔 〕は熱安定化Ce酸化物に付着させたPtの割合	Rh担持量(g/リットル)	Ce-Zr-希土類金属酸化物量(g/リットル)〔 〕はCe/Zr/希土類金属の原子(数)比
1	150	1.0/- [100%]	0.2	74 [5/1/-]
2	150	1.0/- [100%]	0.2	76 [19/1/-]
3	150	1.0/- [100%]	0.2	70 [2/1/-]
4	150	1.0/- [50%]	0.2	74 [5/1/-]
5	150	1.0/- [30%]	0.2	74 [5/1/-]
6	150	1.0/- [100%]	0.2	73 [5/1/0.2] イットリウム
7	150	1.0/- [100%]	0.2	74 [5/1/0.2] イットリウム
A	150	1.0/- [0%]	0.2	74 [5/1/-]
B	150	1.0/- [20%]	0.2	74 [5/1/-]
C	150	1.0/- [100%] アルミナ上	0.2	74 [5/1/-]
D	150	1.0/- [100%] セリア上	0.2	77 [6/-/-]

(Example 8) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m²/g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which

heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0038] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 0.6 % of the weight. Next, the catalyst 8 was acquired like the example 1. A catalyst presentation is shown in a table 2.

[0039] (Example 5 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from gamma-alumina powder, hydrated alumina, and pure water about the multiple oxide powder of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst E was acquired. It is shown in the catalyst presentation table 2.

[0040] (Example 9) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0041] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 5 % of the weight. Next, the catalyst 9 was acquired like the example 1. A catalyst presentation is shown in a table 2.

[0042] (Example 6 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from gamma-alumina powder, hydrated alumina, and pure water about the multiple oxide powder of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst F was acquired. A catalyst presentation is shown in a table 2.

[0043] (Example 10) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0044] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium multiple oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 10.0 % of the weight. Next, the catalyst 10 was acquired like the example 1. A catalyst presentation is shown in a table 2.

[0045] (Example 7 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from gamma-alumina powder, hydrated alumina, and pure water about the multiple oxide powder of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst G was acquired. A catalyst presentation is shown in a table 2.

[0046]

[A table 2]

触媒	アルミナのコート量(g/リットル)	Pt/Pd担持量(g/リットル) []は予めCeに付着させたPtの割合	Rh担持量(g/リットル)	Ce-Zr-希土類金属量(g/リットル) []はCe/Zr-希土類金属の原子(数)比
8	150	0.3/- [100%]	0.1	74 [5/1/-]
E	150	0.3/- [0%]	0.1	74 [5/1/-]
9	150	0.5/- [100%]	0.12	74 [5/1/-]
F	150	0.5/- [0%]	0.12	74 [5/1/-]
10	150	0.5/0.5 100%	0.2	74 [5/1/-]
G	150	0.5/0.5 0%)	0.2	74 [5/1/-]

(Example 11) The catalyst 11 was acquired like the example 1 except having changed gamma-alumina fine particles into the gamma-alumina powder containing Ba of pentatomic % instead of the dinitrodiammine platinum solution used in the example 1 using the dinitrodiammine platinum solution and the palladium nitrate solution. A catalyst presentation is shown in a table 3.

[0047] (Example 8 of a comparison) Catalyst H was acquired like the example 1 of a comparison except having used the palladium nitrate solution instead of the dinitrodiammine platinum solution used in the example 1 of a comparison. It is shown in the catalyst presentation table 3.

(Example 12) The palladium nitrate solution was used instead of the dinitrodiammine platinum solution used in the example 1, and the catalyst 12 was acquired like the example 1 using the gamma-alumina containing La of 3 atom % except having added 0.2 mols /of carbonic acid Bal. by Ba conversion per unit catalyst capacity further. A catalyst presentation is shown in a table 3.

[0048] (Example 9 of a comparison) Catalyst J was acquired like the example 1 except having used the palladium nitrate solution instead of the dinitrodiammine platinum solution used in the example 1. It is shown in the catalyst presentation table 3.

[0049]

[A table 3]

触媒	アルミナのコート量(g/リットル)	Pt/Pd担持量(g/リットル) []は予めCeに付着させたPtの割合	Rh担持量(g/リットル)	Ce-Zr-希土類金属量(g/リットル) []はCe/Zr/希土類金属の原子(数)比
11	150	0.5/0.5 100%	0.2	74 [5/1/-]
H	150	0.5/0.5 0%	0.2	74 [5/1/-]
12	150	-/1.0 (100%)	0.2	74 [5/1/-]
J	150	-/1.0 (0%)	0.2	74 [5/1/-]

(Example 1 of a trial) The exhaust gas temperature of 800 degrees C of average engine-speed 3500rpm and a catalyst inlet port and the exhaust gas temperature of 1050 degrees C of a catalyst center section performed the durability test of 50 hours on the aging conditions which show the catalyst acquired in the example 1 – the example 11 and the example 1 of a comparison – the example 9 of a comparison in installation and drawing 1 at a gasoline engine with a displacement of 4000 cc.

[0050] Aging conditions are the cycles which make 1 cycle 60 seconds as shown in drawing 1, for 40 seconds begun in 1 cycle, when it controls by theoretical-air-fuel-ratio A/F=14.6 and passes over the 40th second, it increases, a fuel is set to A/F=12-13, and the condition is continued for 16 seconds (from the 40th second of 1 cycle to the 56th second). It returns to after that theoretical-air-fuel-ratio A/F=14.6, and engine control is carried out. On the other hand, installation of secondary air does not introduce secondary air as "close" from the start of 1 cycle to the 44th second, but introduces secondary air into the 44th second, and is made "open", and control continued as it is till 60 seconds is carried out. The temperature of a catalyst center section rises from the 44th second of 1 cycle, and it amounts to 1050 degrees C, and becomes the durability test to which temperature descends from 1050 degrees C under hyperoxia from the 55th second.

[0051] Each catalyst which performed the above mentioned durability test evaluated installation and the catalyst engine performance to the gasoline engine with a displacement of 660 cc next. An engine speed is controlled by 3000rpm and theoretical-air-fuel-ratio A/F=14.6, the temperature of a catalyst inlet port is changed, and assessment conditions are HC, CO, and NOx. Clarification temperature was searched for 50%. An assessment result is shown in a table 4 – a table 6.

[0052]

[A table 4]

触媒	担持量 (g／1)		耐久後 50% 清化温度 (°C)		
	Pt	Rh	HC	CO	NOx
1	1. 0	0. 2	381	371	369
2	1. 0	0. 2	384	373	372
3	1. 0	0. 2	389	378	378
4	1. 0	0. 2	384	374	373
5	1. 0	0. 2	388	376	375
6	1. 0	0. 2	380	367	365
7	1. 0	0. 2	382	372	374
A	1. 0	0. 2	402	393	391
B	1. 0	0. 2	395	386	384
C	1. 0	0. 2	411	418	416
D	1. 0	0. 2	405	396	393

As for the catalysts 1-7 of the example of this invention, from a table 4, 367 degrees C - 378 degrees C and 50% clarification temperature after durability of NOx have [50% clarification temperature after durability of HC] 381 degrees C - 389 degrees C and 50% clarification temperature after durability of CO in the range which is 365 degrees C - 378 degrees C. On the other hand, as for catalyst A-D of the example of a comparison, 386 degrees C - 418 degrees C and 50% clarification temperature after durability of NOx have [50% clarification temperature after durability of HC] 395 degrees C - 411 degrees C and 50% clarification temperature after durability of CO in the range which is 384 degrees C - 416 degrees C.

[0053] At catalyst A-D of the catalysts 1-7 of the example of this invention, and the example of a comparison, clarification temperature averages after [durability] 50%, by HC, 29 degrees of catalysts 1-7 of the example of this invention are by 13 degrees C and CO, and 28 degrees C and all are low by NOx. That is, the catalysts 1-7 of the example of this invention have high endurance, and are understood that catalytic activity is maintained so much highly.

[0054]

[A table 5]

触媒	担持量 (g／1)		耐久後50%净化温度 (℃)		
	Pt	Rh	HC	CO	NOx
8	0.3	0.1	421	424	416
E	0.3	0.1	449	452	443
9	3.0	0.3	398	396	380
F	3.0	0.3	428	425	414
10	5.0	0.5	415	408	406
G	5.0	0.5	436	422	423

The catalyst 8, the catalyst 9, and catalyst 10 of an example of this invention have low 50% clarification temperature after durability like [the result of a table 5] the result of a table 4 as compared with Catalyst E, Catalyst F, and Catalyst G of the example of a comparison. That is, it turns out that the catalyst 8, the catalyst 9, and catalyst 10 of an example of this invention are all excellent in endurance ability.

[0055]

[A table 6]

触媒	担持量 (g／1)			耐久後50%净化温度 ()		
	Pt	Pd	Rh	HC	CO	NOx
11	0.5	0.5	0.2	415	408	406
H	0.5	0.5	0.2	436	422	423
12	—	1.0	0.2	431	432	433
J	—	1.0	0.2	453	451	454

The catalyst 11 and catalyst 12 of an example of this invention have low 50% clarification temperature after durability like [the result of a table 6] the result of a table 4 and a table 5 as compared with Catalyst H, Catalyst F, and Catalyst J of the example of a comparison. That is, it turns out that the catalyst 11 and catalyst 12 of an example of this invention are all excellent in endurance ability.

(Example 2 of a trial) The palladium particle diameter after the durability of the catalyst of the platinum particle diameter after the durability of the catalyst of an example 1 and the example 1 of a comparison, an example 11, and the example 8 of a comparison was measured by XRD (X diffraction). A garden result is shown in the 7th table.

[0056]

[A table 7]

	Pt粒子径(Å)		Pd粒子径(Å)
触媒1	98	触媒11	205
触媒A	202	触媒H	317

The catalyst 1 for exhaust gas clarification and catalyst 11 of this invention have the diameter of a very fine particle of platinum and palladium smaller than the thing of the catalyst A of the example of a comparison, and Catalyst H from a table 7. Thereby, as for the catalyst 1 for exhaust gas clarification and catalyst 2 of this invention, it turns out that sintering of platinum and palladium is controlled.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The cycle diagram showing the engine drive of the aging (aging) trial made to each catalyst of the example of this invention, and the example of a comparison.

[Translation done.]

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(54)【発明の名称】排気ガス浄化用触媒

(57)【要約】

【目的】耐久性の高い内燃機関用三元触媒を提供する。

【構成】ジルコニウムまたはセリウムを除く希土類金属とジルコニウムとで安定化されたセリウム酸化物に白金および/またはパラジウムを担持した触媒活性成分と、活性アルミニナを主体とした耐火性無機酸化物よりなる混合物を触媒担体に被覆せしめた後、更にロジウムおよび/またはロジウムと白金族金属とを担持してなる事を特徴とする。白金およびパラジウムが安定化されたセリウムに予め担持されているため、白金、パラジウムのシナクリングが抑制され、触媒活性が長く維持できる。

(七) 72/1217-T2-7

【特許請求の範囲】

【請求項1】ジルコニウムまたはセリウムを除く希土類金属とジルコニウムとで熱安定化されたセリウム酸化物に白金および／またはパラジウムを担持した触媒活性成分と、活性アルミナを主体とした耐火性無機酸化物よりなる混合物を触媒担体に被覆せしめた後、更にロジウムおよび／またはロジウムと白金族金属とを担持してなる事を特徴とする排気ガス浄化用触媒。

【請求項2】担持されている白金および／またはパラジウムの総量の少なくとも30重量%以上が熱安定化されたセリウム酸化物に担持されている請求項1記載の排気ガス浄化用触媒。

【請求項3】触媒の単位容量当たり白金および／またはパラジウムの担持量が0.1～5.0g／リットルであり、ロジウムの担持量が0.01～1.0g／リットルである請求項1記載の排気ガス浄化用触媒。

【請求項4】触媒の単位容量当たり白金および／またはパラジウムの担持量が0.3～3.0g／リットルであり、ロジウムの担持量が0.05～0.5g／リットルである請求項1記載の排気ガス浄化用触媒。

【請求項5】ロジウムの50重量%以上は触媒担体に被覆された耐火性無機酸化物よりなる層の表面より40μm以内に担持されている請求項1記載の排気ガス浄化用触媒。

【請求項6】触媒担体1リットル当たり、熱安定化されたセリウム酸化物が10～200gおよび耐火性無機酸化物が80～300gである請求項1記載の排気ガス浄化用触媒。

【請求項7】熱安定化されたセリウム酸化物の平均粒径は10μm以下、比表面積は20m²/g以上である請求項1記載の排気ガス浄化用触媒。

【請求項8】熱安定化されたセリウム酸化物は、セリウム酸化物と、ジルコニウム酸化物と、セリウム酸化物を除く希土類酸化物の混合物で、少なくとも一部が複合酸化物または固溶体として存在している請求項1記載の排気ガス浄化用触媒。

【請求項9】セリウム酸化物、ジルコニウム酸化物および希土類酸化物の複合酸化物または固溶体は、原子割合で各々ジルコニウムが0.05～0.35、希土類金属が0～0.30、ジルコニウムと希土類金属の合計が0.05～0.55で残部がセリウムとなるように構成されている請求項5記載の排気ガス浄化用触媒。

【請求項10】耐火性無機酸化物は、活性アルミナ、熱安定化された活性アルミナ、希土類金属の酸化物、アルカリ土類金属の酸化物である請求項1記載の排気ガス浄化用触媒。

【請求項11】活性アルミナはγ-アルミナ、δ-アルミナ、θアルミナの一種またはこれらの混合物で、平均粒径が10μm以下、比表面積が50m²/g以上である請求項1記載の排気ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、排気ガス浄化用触媒に関するもので、自動車等の内燃機関からの排気ガス中に含まれる有害成分である一酸化炭素(CO)、炭化水素(HC)および窒素酸化物(NOx)を同時に除去する排気ガス浄化用触媒に関するものである。

【0002】

【従来の技術】従来、内燃機関から排出される排気ガス中の有害成分である一酸化炭素、炭化水素および窒素酸化物を同時に除去する三元触媒では、主として白金、ロジウム等の白金族元素および低温活性向上のために酸素貯蔵効果を持つ酸化セリウムが用いられている。

【0003】このような従来の排気ガス浄化用触媒は、一体構造型モノリス担体に、活性アルミナのスラリーでコーティングを行い、その後セリウム溶液に含浸し、更にその後白金、ロジウム等の白金族元素含有溶液を用いて、含浸担持を行っている。最近、それら触媒の設置場所が、よりエンジンに近いマニホールド直下とされる傾向があることや、また高速運転時における排気ガス温度の上昇等により、触媒の高温耐熱性がより大きく要求されてきた。

【0004】しかし、従来の白金族元素や酸化セリウムを含む触媒は、高温において劣化され易い。この為、触媒の高温耐熱性を向上させるために、希土類金属やアルカリ土類金属の酸化物を添加している。また、高温で長時間使用すると白金粒子が凝集して粒成長を起こすいわゆるシントーリングが発生して浄化性能が著しく劣化する。実公平5-20435号公報に白金のシントーリング抑制のため酸化セリウム上に白金を担持した触媒が開示されている。

【0005】

【発明が解決しようとする課題】しかしながら、上記した従来の三元触媒は、初期においてはCO、HCおよびNOxの3成分を浄化するための良好な三元活性を示すものの、マニホールド直下のような高温かつガス雰囲気成分の変動の大きい部分では、耐久性や耐熱性においては必ずしも十分であるとはいえないかった。

【0006】したがって、本発明は、触媒成分として白金および／またはパラジウムとロジウムとを使用する触媒において、CO、HCおよびNOxの3成分を同時に初期から長期にわたって安定して浄化し、高温での耐久性を維持できる触媒を提供することにある。

【0007】

【課題を解決するための手段】本発明者は、この課題を解決するために鋭意研究した結果、ジルコニウムまたはセリウムを除く希土類金属とジルコニウムとで熱安定化されたセリウム酸化物に白金および／またはパラジウムを担持した触媒活性成分と、活性アルミナを主体とした耐火性無機酸化物よりなる混合物を触媒担体に被覆せし

めた後、更にロジウムおよび／またはロジウムと白金族金属とを担持してなる排気ガス浄化用触媒が、従来の白金および／またはパラジウムとロジウムとを含む触媒に比べ触媒性能が向上することを見出し、本発明を完成するに至ったものである。

【0008】触媒活性成分や耐火性無機酸化物に担持される白金および／またはパラジウムの担持量は、触媒の単位容量当り0.1～5.0g／リットルであることが好ましい。白金および／またはパラジウムの担持量が単位容量当り0.1g／リットル未満の場合、十分な浄化性能が得られない恐れがある。また逆に、白金および／またはパラジウムの担持量が単位容量当り5.0g／リットルを超えても担持量に見合うだけの効果が得られない。特に、白金および／またはパラジウムの担持量が単位容量当り0.3～3.0g／リットルである場合が触媒活性とコストの面より好ましい。

【0009】また、触媒担体に担持される白金および／またはパラジウムの全担持量の30重量%以上が、熱安定化セリウム酸化物に担持されるのが好ましい。それは白金および／またはパラジウムの担持量が30%未満の場合、高温時のシンタリング抑制が十分でないため、好ましくない。触媒担体に担持されるロジウムの担持量は、触媒の単位容積当り0.01～1.0g／リットルであることが好ましい。それはロジウムの担持量が単位容積当り0.01g／リットル未満の場合、十分な触媒活性が得られない恐れがある。また逆に、ロジウムの担持量が単位容積当り1.0g／リットルを超えても担持量に見合うだけの効果が得られない。特に、ロジウムの担持量が単位容積当り0.05～0.5g／リットルである場合は、触媒活性とコストの面でより好ましい。

【0010】耐火性無機酸化物としては、活性アルミニナ、シリコンおよび／またはそれらの酸化物で熱安定化された活性アルミニナ、ランタン等の希土類金属の酸化物、マグネシウム、バリウム等のアルカリ土類金属の酸化物が好ましい。これらの耐火性無機酸化物は粒径の小さい、比表面積の大きいものが好ましい。活性アルミニナの場合は平均粒径が10μm以下、比表面積が50m²／g以上が良い。

【0011】具体的には、耐火性無機酸化物は活性アルミニナを主体とするものが良い。より好ましくは、耐火性無機酸化物は、活性アルミニナに希土類金属の酸化物もしくは化合物、アルカリ土類金属の酸化物あるいは化合物の一種以上を含むものが良い。また活性アルミニナはγ-アルミニナ、δ-アルミニナ、θ-アルミニナの一種またはこれらの混合物からなり、更に好ましくは熱安定化のためにシリコン、希土類金属、アルカリ土類金属の一種またはその化合物を含むものが良い。

【0012】熱安定化されたセリウム酸化物はジルコニウムまたはセリウムを除く希土類金属とジルコニウム上で熱安定化されている。この熱安定化されたセリウム酸

化物（以下、熱安定化セリウム酸化物という）は以下の方法で調整することができる。しかし、熱安定化セリウム酸化物はここに示される調整方法に特に限定されるものではない。この熱安定化セリウム酸化物の調整方法として、市販の酸化セリウムに水可溶性のジルコニウム塩および／またはセリウムを除く希土類金属塩を担持する方法、水に溶かしたセリウム塩、ジルコニウム塩および／またはセリウムを除く希土類金属塩を混合し乾燥後、焼成する方法、水可溶性のセリウム塩、ジルコニウム塩および／またはセリウムを除く希土類金属を混合後、耐火性無機酸化物に担持する方法等をあげることができる。なお、焼成は例えば空気中で500℃、5時間程度加熱することによりなされる。いずれの方法でも、用いるセリウム、ジルコニウムおよびセリウムを除く希土類金属の各塩は特に限定されず、市販の硝酸塩、酢酸塩、硫酸塩、塩化物等を用いることができる。

【0013】前記調整方法にて調整された熱安定化セリウム酸化物は、セリウム酸化物と、ジルコニウム酸化物とセリウム酸化物を除いた希土類酸化物との混合物で、

10 少なくとも一部が複合酸化物または固溶体として存在している。熱安定化セリウム酸化物を構成するセリウム原子、ジルコニウム原子およびセリウム原子以外の希土類元素の原子の割合は、全体を100原子%としたとき、ジルコニウム原子が5～35原子%、セリウム原子以外の希土類元素の原子が0～30原子%、残部がセリウム原子となるのが好ましい。

【0014】上記の方法で調整された熱安定化セリウム酸化物を空気中で900℃にて5時間焼成しても比表面積が20m²／g以上である。なお、市販の酸化セリウムは同条件で焼成すると比表面積は10m²／g以下に劣化する。上記の如く混合される各成分は、触媒1リットル当たり、熱安定化セリウム酸化物が1.0～2.0gおよび耐火性無機酸化物が8.0～30.0gの割合で配合されるのが好ましい。

30 【0015】触媒活性成分と耐火性無機酸化物の混合物を被覆された触媒担体は、更に触媒金属を担持させるが、その触媒金属としては熱安定化セリウム酸化物に既に担持された白金および／またはパラジウムや、ロジウム等の白金族金属やその他貴金属のこと、1種または2種以上用いて担持するのが好ましい。

40 【0016】
【発明の作用および効果】本発明は、白金および／またはパラジウムが熱安定化セリウム酸化物上に担持されているため、従来解決できなかったシンタリングを抑制することができた。そのため、マニホールド直下のような高温でかつガス雰囲気の変動の大きい場所においても、耐久性と耐熱性とを大きく改善することができた。

【0017】また、熱安定化セリウム酸化物上にある白金および／またはパラジウムは、従来方法での活性アルミニナ上にある白金および／またはパラジウムに比べ、C

O_xおよびNO_x成分の浄化率が向上した。また、熱安定化されないセリウム酸化物上にある白金、パラジウムに比較し、本発明の熱安定化したセリウム酸化物上にある白金、パラジウムは耐久性が著しく向上している。また本発明の本発明の熱安定化したセリウム酸化物は白金、パラジウムをセリウム塩とともに混合、酸化したものに比べ、少量の白金、パラジウムでより優れたCO_x、およびNO_xの浄化ができた。

【0018】

【実施例】以下、実施例により具体的に説明する。

(実施例1) 平均粒径5μmで、比表面積120m²/gの酸化セリウムとオキシ硝酸ジルコニウム溶液を混合し、乾燥後、500℃の温度で1時間焼成してジルコニウムで熱安定化されたセリウム複合酸化物粉末を得た。このジルコニウムで熱安定化されたセリウム複合酸化物の組成は、セリウム/ジルコニウムのモル比で5/1であった。

【0019】次に、上記ジルコニウムで熱安定化されたセリウム複合酸化物粉末にジニトロジアンミン白金溶液を添加し、乾燥後、500℃の温度で1時間焼成して白金含有ジルコニウムーセリウム複合酸化物中の白金含有量は2重量%であった。次に、400セル/in²、直径80mm、長さ95mmのコーディエライト製のモノリス担体に、白金含有ジルコニウムーセリウムの複合酸化物粉末、セリウムジルコニウムの複合酸化物粉末、γアルミナ粉末、アルミナ水和物および純水からなるスラリーをコートし、乾燥後、500℃の温度で1時間焼成して、コーディエライト製のモノリス担体に、白金、セリウム、ジルコニウムおよび活性アルミナ含有層を形成した。

【0020】更に、このモノリス担体を硝酸ロジウム溶液に浸漬してロジウムを担持して触媒1を得た。触媒組成を表1に示す。また、この触媒1の被覆層断面をE.P.M.A (electron probe microanalysis)で白金、セリウムおよびロジウムの配合割合を調べた。この結果、ロジウムは被覆層の表面より40μmの範囲に存在した。また、白金とセリウムはピーク等が類似した組成をもつことが明らかになった。このことより白金とセリウムが互いに近接して存在することがわかる。

【0021】(実施例2) セリウム/ジルコニウムのモル比を19/1に変え、γアルミナ粉末を3原子%のLaを含むγアルミナ粉末に変えた以外は、実施例1と同様にして触媒1を得た。触媒組成を表1に示す。

(実施例3) セリウム/ジルコニウムのモル比を2/1に変え、γアルミナ粉末を3原子%のBaを含むγアルミナ粉末に変えた以外は、実施例1と同様にして触媒1を得た。触媒組成を表1に示す。

【0022】(実施例4) 実施例1の白金含有ジルコニウムーセリウム複合酸化物中の白金含有量の2.0重量

%を1.0重量%にし、実施例1と同様にしてモノリス担体に、白金含有ジルコニウムーセリウム複合酸化物と活性アルミナとよりなる被覆層を形成した。

【0023】更に、この被覆層をもつモノリス担体をジニトロジアンミン白金溶液に浸漬後、乾燥し、更に硝酸ロジウム溶液に浸漬してロジウムを担持して触媒4を得た。触媒組成を表1に示す。

(実施例5) 実施例1の白金含有ジルコニウムーセリウム複合酸化物中の白金含有量の2.0重量%を0.6重量%にし、実施例1と同様にしてモノリス担体に、白金含有ジルコニウムーセリウム複合酸化物と活性アルミナとよりなる被覆層を形成した。

【0024】更に、この被覆層をもつモノリス担体をジニトロジアンミン白金溶液に浸漬後、乾燥し、更にその後硝酸ロジウム溶液に浸漬してロジウムを担持して触媒5を得た。触媒組成を表1に示す。

(実施例6) 平均粒径5μmで、比表面積120m²/gの酸化セリウムとオキシ硝酸ジルコニウム溶液および硝酸イットリウム溶液を混合し、乾燥後、500℃の温

度で1時間焼成してジルコニウムおよびイットリウムで熱安定化されたセリウム複合酸化物粉末を得た。このジルコニウムおよびイットリウムで熱安定化されたセリウム複合酸化物の組成は、セリウム/ジルコニウム/イットリウムのモル比で5/1/0.2であった。

【0025】次に、上記ジルコニウムおよびイットリウムで熱安定化されたセリウム複合酸化物粉末にジニトロジアンミン白金溶液を添加し、乾燥後、500℃の温度で1時間焼成して白金含有ジルコニウムーイットリウムーセリウム複合酸化物を得た。この白金含有ジルコニウムーイットリウムーセリウム複合酸化物中の白金含有量は2重量%であった。

【0026】次に、400セル/in²、直径80mm、長さ95mmのコーディエライト製のモノリス担体に、白金含有ジルコニウムーイットリウムーセリウムの複合酸化物粉末、セリウムジルコニウムの複合酸化物粉末、γアルミナ粉末、アルミナ水和物および純水からなるスラリーをコートし、乾燥後、500℃の温度で1時間焼成して、モノリス担体に、白金、セリウム、ジルコニウム、イットリウムおよび活性アルミナを含む層を形成した。

【0027】更に、このモノリス担体を硝酸ロジウム溶液に浸漬してロジウムを担持して触媒6を得た。触媒組成を表1に示す。

(実施例7) 平均粒径5μmで、比表面積120m²/gの酸化セリウムとオキシ硝酸ジルコニウム溶液および硝酸イットリビウム溶液を混合し、乾燥後、500℃の温度で1時間焼成してジルコニウムおよびイットリビウムで熱安定化されたセリウム複合酸化物粉末を得た。このジルコニウムおよびイットリビウムで熱安定化されたセリウム複合酸化物の組成は、セリウム/ジルコニウム

/イッテルビウムのモル比で5/1/0.2であった。
【0028】次に、ジルコニウムおよびイッテルビウムで熱安定化されたセリウム複合酸化物粉末にジニトロジアンミン白金溶液を添加し、乾燥後、500℃の温度で1時間焼成して白金含有ジルコニウムーイッテルビウムーセリウム複合酸化物を得た。この白金含有ジルコニウムーイッテルビウムーセリウム複合酸化物中の白金含有量は2重量%であった。

【0029】次に、400セル/ 1m^2 、直径80m
m、長さ95mmのコーディエライト製のモノリス担体
に、白金含有ジルコニウムーイッテルビウムーセリウム
の複合酸化物粉末、セリウムージルコニウムの複合酸
化物粉末、 γ -アルミナ粉末、アルミナ水和物および純水
からなるスラリーをコートし乾燥後、500℃の温度で
1時間焼成して、モノリス担体に、白金、セリウム、ジ
ルコニウム、イッテルビウムおよび活性アルミナを含む
層を形成した。

【0030】更に、このモノリス担体を硝酸ロジウム溶
液に浸漬してロジウムを担持して触媒7を得た。触媒組
成を表1に示す。

(比較例1) 実施例1と同様のコーディエライト製のモ
ノリス担体に、セリウムージルコニウムの複合酸化物粉
末と γ -アルミナ粉末、アルミナ水和物および純水から
なるスラリーをコートし、乾燥後、500℃の温度で1
時間焼成して、コーディエライト製のモノリス担体上に
セリウムージルコニウムを含有するアルミナ層を形成した。
このようにして得たモノリス担体を、ジニトロジ
アンミン白金溶液に浸漬後、乾燥し、更に硝酸ロジウム溶
液に浸漬してロジウムを担持して触媒Aを得た。触媒組
成を表1に示す。この触媒Aの被覆層断面をEPMAで
白金およびロジウムの配合割合を調べた。この結果、白
金は被覆層の表面より100μmの範囲に、ロジウムは被
覆層の表面より40μmの範囲に分布していた。

【0031】(比較例2) 実施例1の白金含有ジルコニ
ウムーセリウム複合酸化物中の白金含有量の2.0重量
%を0.4重量%にし、実施例1と同様にしてコーディ

エライト製のモノリス担体に、白金、セリウム、ジルコ
ニウムおよび活性アルミナよりなる層を形成した。

【0032】更に、このモノリス担体をジニトロジアン
ミン白金溶液に浸漬後、乾燥し、更に硝酸ロジウム溶液
に浸漬してロジウムを担持して触媒Bを得た。触媒組成
を表1に示す。

(比較例3) 活性アルミナ粉末にジニトロジアンミン白
金溶液を添加し、乾燥、焼成して白金含有活性アルミナ
を得た。この白金含有活性アルミナ中の白金含有量は
2.0重量%であった。

【0033】次に、実施例1と同様のコーディエライト
製のモノリス担体に、白金含有活性アルミナ、セリウム
ージルコニウムの複合酸化物粉末、 γ -アルミナ粉末、
アルミナ水和物および純水からなるスラリーをコート
し、乾燥後、500℃の温度で1時間焼成して、コーデ
ィエライト製のモノリス担体に、白金、セリウム、ジル
コニウムおよび活性アルミナを含む層を形成した。

【0034】更に、このモノリス担体を硝酸ロジウム溶
液に浸漬してロジウムを担持して触媒Cを得た。触媒組
成を表1に示す。

(比較例4) 酸化セリウム粉末にジニトロジアンミン白
金溶液を添加し、乾燥、焼成して白金含有酸化セリウム
を得た。この白金含有酸化セリウム中の白金含有量は
2.0重量%であった。

【0035】次に、実施例1と同様のコーディエライト
製のモノリス担体に、白金含有酸化セリウム、セリウム
ージルコニウムの複合酸化物粉末、 γ -アルミナ粉末、
アルミナ水和物および純水からなるスラリーをコート
し、乾燥後、500℃の温度で1時間焼成して、コーデ
ィエライト製のモノリス担体に、白金、セリウム、ジル
コニウムおよび活性アルミナを含む層を形成した。

【0036】更に、このモノリス担体を硝酸ロジウム溶
液に浸漬してロジウムを担持して触媒Dを得た。触媒組
成を表1に示す。

【0037】

【表1】

触媒	アルミナのコート量(g/リットル)	Pt/Pd担持量(g/リットル) []は熱安定化Ce酸化物に付着させたPtの割合	Rh担持量(g/リットル)	Ce-Zr-希土類金属酸化物量(g/リットル) []はCe/Zr/希土類金属の原子(数)比
1	150	1.0/- [100%]	0.2	74 [5/1/-]
2	150	1.0/- [100%]	0.2	76 [19/1/-]
3	150	1.0/- [100%]	0.2	70 [2/1/-]
4	150	1.0/- [50%]	0.2	74 [5/1/-]
5	150	1.0/- [30%]	0.2	74 [5/1/-]
6	150	1.0/- [100%]	0.2	73 [5/1/0.2] イットリウム
7	150	1.0/- [100%]	0.2	74 [5/1/0.2] イットリウム
A	150	1.0/- [0%]	0.2	74 [5/1/-]
B	150	1.0/- [20%]	0.2	74 [5/1/-]
C	150	1.0/- [100%] アルミナ上	0.2	74 [5/1/-]
D	150	1.0/- [100%] セリア上	0.2	77 [6/-/-]

(実施例8) 平均粒径5μmで、比表面積120m²/gの酸化セリウムとオキシ硝酸ジルコニウム溶液を混合し、乾燥後、500℃の温度で1時間焼成してジルコニウムで熱安定化されたセリウム複合酸化物粉末を得た。このジルコニウムで熱安定化されたセリウム複合酸化物の組成は、セリウム/ジルコニウムのモル比で5/1であった。

【0038】次に、上記ジルコニウムで熱安定化されたセリウム複合酸化物粉末にジニトロジアンミン白金溶液を添加し、乾燥後、500℃の温度で1時間焼成して白金含有ジルコニウムーセリウム複合酸化物を得た。この白金含有ジルコニウムーセリウム複合酸化物中の白金含有量は0.6重量%であった。次に、実施例1と同様にして触媒8を得た。触媒組成を表2に示す。

【0039】(比較例5) 実施例1と同様のコーディエライト製のモノリス担体に、セリウムジルコニウムの複合酸化物粉末を、γ-アルミナ粉末、アルミナ水和物および純水からなるスラリーをコートし、乾燥後、50

0℃の温度で1時間焼成して、コーディエライト製のモノリス担体上にセリウムジルコニウムを含有するアルミナ層を形成した。このようにして得たモノリス担体を、ジニトロジアンミン白金溶液に浸漬後、乾燥し、更に硝酸ロジウム溶液に浸漬してロジウムを担持して触媒Eを得た。触媒組成表2に示す。

【0040】(実施例9) 平均粒径5μmで、比表面積120m²/gの酸化セリウムとオキシ硝酸ジルコニウム溶液を混合し、乾燥後、500℃の温度で1時間焼成してジルコニウムで熱安定化されたセリウム複合酸化物粉末を得た。このジルコニウムで熱安定化されたセリウム複合酸化物の組成は、セリウム/ジルコニウムのモル比で5/1であった。

【0041】次に、上記ジルコニウムで熱安定化されたセリウム複合酸化物粉末にジニトロジアンミン白金溶液を添加し、乾燥後、500℃の温度で1時間焼成して白金含有ジルコニウムーセリウム複合酸化物を得た。この白金含有ジルコニウムーセリウム複合酸化物中の白金含有量

は5重量%であった。次に、実施例1と同様にして触媒9を得た。触媒組成を表2に示す。

【0042】(比較例6)実施例1と同様のコーディエライト製のモノリス担体に、セリウムジルコニウムの複合酸化物粉末を、ヤーアルミナ粉末、アルミナ水和物および純水からなるスラリーをコートし、乾燥後、500℃の温度で1時間焼成して、コーディエライト製のモノリス担体上にセリウムジルコニウムを含有するアルミナ層を形成した。このようにして得たモノリス担体を、ジニトロジアンミン白金溶液に浸漬後、乾燥し、更に硝酸ロジウム溶液に浸漬してロジウムを担持して触媒Fを得た。触媒組成を表2に示す。

【0043】(実施例10)平均粒径5μmで、比表面積120m²/gの酸化セリウムとオキシ硝酸ジルコニウム溶液を混合し、乾燥後、500℃の温度で1時間焼成してジルコニウムで熱安定化されたセリウム複合酸化物粉末を得た。このジルコニウムで熱安定化されたセリウム複合酸化物の組成は、セリウム/ジルコニウムのモル比で5/1であった。

*

*【0044】次に、上記ジルコニウムで熱安定化されたセリウム複合酸化物粉末にジニトロジアンミン白金溶液を添加し、乾燥後、500℃の温度で1時間焼成して白金含有ジルコニウム—セリウム複合酸化物を得た。この白金含有ジルコニウム—セリウム複合酸化物中の白金含有量は10.0重量%であった。次に、実施例1と同様にして触媒10を得た。触媒組成を表2に示す。

【0045】(比較例7)実施例1と同様のコーディエライト製のモノリス担体に、セリウムジルコニウムの複合酸化物粉末を、ヤーアルミナ粉末、アルミナ水和物および純水からなるスラリーをコートし、乾燥後、500℃の温度で1時間焼成して、コーディエライト製のモノリス担体上にセリウムジルコニウムを含有するアルミナ層を形成した。このようにして得たモノリス担体を、ジニトロジアンミン白金溶液に浸漬後、乾燥し、更に硝酸ロジウム溶液に浸漬してロジウムを担持して触媒Gを得た。触媒組成を表2に示す。

【0046】

【表2】

触媒	アルミナのコート量(g/リットル)	Pt/Pd担持量(g/リットル)〔PtはCeに付着させたPtの割合〕	Rh担持量(g/リットル)	Ce-Zr-希土類金属量(g/リットル)〔RhはCe/Zr/希土類金属の原子(数)比〕
8	150	0.3/- [100%]	0.1	74 [5/1/-]
E	150	0.3/- [0%]	0.1	74 [5/1/-]
9	150	0.5/- [100%]	0.12	74 [5/1/-]
F	150	0.5/- [0%]	0.12	74 [5/1/-]
10	150	0.5/0.5 100%	0.2	74 [5/1/-]
G	150	0.5/0.5 0%	0.2	74 [5/1/-]

(実施例11)実施例1で使用したジニトロジアンミン白金溶液の代わりにジニトロジアンミン白金溶液と硝酸バラジウム溶液を使用し、ヤーアルミナ粉体を5原子%のBaを含むヤーアルミナ粉末に変えた以外は、実施例1と同様にして触媒11を得た。触媒組成を表3に示す。

【0047】(比較例8)比較例1で使用したジニトロジアンミン白金溶液の代わりに硝酸バラジウム溶液を使用した以外は、比較例1と同様にして、触媒Hを得た。触媒組成表3に示す。

(実施例12)実施例1で使用したジニトロジアンミン白金溶液の代わりに硝酸バラジウム溶液を使用し、3原

子%のLaを含むヤーアルミナを用い、さらに炭酸Baを単位触媒容量当たりBa換算で0.2mol/l加えた以外は、実施例1と同様にして触媒12を得た。触媒組成を表3に示す。

【0048】(比較例9)実施例1で使用したジニトロジアンミン白金溶液の代わりに硝酸バラジウム溶液を使用した以外は、実施例1と同様にして、触媒Jを得た。触媒組成表3に示す。

【0049】

【表3】

触媒	アルミナのコート量(g/リットル)	Pt/Pd担持量(g/リットル) []は予めCeに付着させたPtの割合	Rh 搅持量(g/リットル)	Ce-Zr-希土類金属量(g/リットル) []はCe/Zr/希土類金属の原子(数)比
11	150	0.5/0.5 100%	0.2	74 [5/1/-]
H	150	0.5/0.5 0%	0.2	74 [5/1/-]
12	150	-/1.0 [100%]	0.2	74 [5/1/-]
J	150	-/1.0 [0%]	0.2	74 [5/1/-]

(試験例1) 実施例1～実施例11および比較例1～比較例9で得られた触媒を排気量4000ccのガソリンエンジンに取り付け、第1図に示すエージング条件で、平均のエンジン回転数3500rpm、触媒入口の排気ガス温度800°C、触媒中央部の排気ガス温度1050°Cで50時間の耐久試験を行った。

【0050】エージング条件は第1図に示すように、1サイクルを60秒とするサイクルで、1サイクル中の始めの40秒は、理論空燃比A/F=14.6で制御し、40秒目を過ぎたときに、燃料を増大しA/F=12～13とし、その状態を16秒（1サイクルの40秒目から56秒目まで）続ける。その後理論空燃比A/F=14.6に戻してエンジン制御する。一方、2次空気の導入は、1サイクルの始めから44秒目まで「閉」として

2次空気を導入せず、44秒目に2次空気を導入し「開」とし、そのまま60秒まで続ける制御をするものである。1サイクルの44秒目から触媒中央部の温度が上昇し、1050°Cに達し、55秒目からは酸素過剰下で1050°Cから温度が下降する耐久試験となる。

20 【0051】前記した耐久試験を行った各触媒は、次に排気量660ccのガソリンエンジンに取り付け、触媒性能を評価した。評価条件はエンジン回転数を3000rpm、理論空燃比A/F=14.6で制御し、触媒入口の温度を変化させて、HC、COおよびNO_xの50%浄化温度を求めた。評価結果を表4～表6に示す。

【0052】
【表4】

触媒	担持量 (g/1)		耐久後50%浄化温度 (°C)		
	Pt	Rh	HC	CO	NOx
1	1.0	0.2	381	371	369
2	1.0	0.2	384	373	372
3	1.0	0.2	389	378	378
4	1.0	0.2	384	374	373
5	1.0	0.2	388	376	375
6	1.0	0.2	380	367	365
7	1.0	0.2	382	372	374
A	1.0	0.2	402	393	391
B	1.0	0.2	395	386	384
C	1.0	0.2	411	418	416
D	1.0	0.2	405	396	393

表4より、本発明の実施例の触媒1～7は、HCの耐久後50%浄化温度が381°C～389°C、COの耐久後50%浄化温度が367°C～378°C、NOxの耐久後50%浄化温度が365°C～378°Cの範囲にある。一方、比較例の触媒A～Dは、HCの耐久後50%浄化温度が395°C～411°C、COの耐久後50%浄化温度が386°C～418°C、NOxの耐久後50%浄化温度が384°C～416°Cの範囲にある。

【0053】本発明の実施例の触媒1～7と比較例の触媒A～Dでは、耐久後50%浄化温度が平均して、HCで13°C、COで29°C、NOxで28°C、いずれも本発明の実施例の触媒1～7が低くなっている。すなわち、本発明の実施例の触媒1～7は耐久性が高く、それだけ触媒活性が高く維持されているのがわかる。

【0054】

【表5】

触媒	担持量 (g/1)		耐久後 50% 清化温度 (°C)		
	Pt	Rh	HC	CO	NOx
8	0.3	0.1	421	424	416
E	0.3	0.1	449	452	443
9	3.0	0.3	398	396	380
F	3.0	0.3	428	425	414
10	5.0	0.5	415	408	406
G	5.0	0.5	436	422	423

表5の結果も、表4の結果と同様、本発明の実施例の触媒8、触媒9および触媒10は、比較例の触媒E、触媒Fおよび触媒Gに比較し、耐久後50%清化温度が低い。すなわち、本発明の実施例の触媒8、触媒9および*

*触媒10はいずれも耐久性能が優れていることが判る。
【0055】

20 【表6】

触媒	担持量 (g/1)			耐久後 50% 清化温度 ()		
	Pt	Pd	Rh	HC	CO	NOx
11	0.5	0.5	0.2	415	408	406
H	0.5	0.5	0.2	436	422	423
12	-	1.0	0.2	431	432	433
J	-	1.0	0.2	453	451	454

表6の結果も、表4、表5の結果と同様、本発明の実施例の触媒11および触媒12は、比較例の触媒H、触媒Fおよび触媒Jに比較し、耐久後50%清化温度が低い。すなわち、本発明の実施例の触媒11および触媒12はいずれも耐久性能が優れていることが判る。

(試験例2) 実施例1および比較例1の触媒の耐久後の※40

	Pt粒子径 (Å)		Pd粒子径 (Å)
触媒1	98	触媒11	205
触媒A	202	触媒H	317

表7より、本発明の排気ガス浄化用触媒1および触媒11は、白金およびパラジウムの微細粒子径が比較例の触媒Aおよび触媒Hのものより小さい。これにより、本発

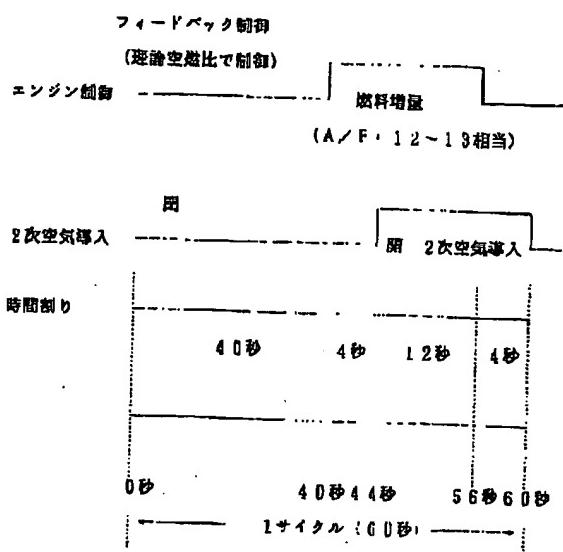
明の排気ガス浄化用触媒1および触媒2は、白金およびパラジウムのシントリングが抑制されていることがわかる。

【図面の簡単な説明】

【図1】本発明の実施例および比較例の各触媒に対して

なされた老化（エーティング）試験の、エンジン駆動を示すサイクル線図。

【図1】



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